BCHM 485 Answers/Solutions to Exam #1 problems Spring 2025

Problem 1. (This is a conceptual question.) Consider a quantum mechanical system in a superposition state in which the wave function $\Psi(x, t)$ is a linear combination of two wave functions each corresponding to a stationary state as specified below. Assume arbitrary nonzero projection coefficients (b_1 and b_2). *Is this superposition state a stationary state?* Answer this question for the following two cases. Explain your reasoning and support your answer by equations/calculations. *Reminder*: in the stationary state the probability density is time independent.

A stationary state is the state where the probability density is time independent. Therefore, to answer this question you need to consider/calculate the probability density using time-dependent form of the wave function in question. This means that for the individual wave functions you need to use solutions for the time-dependent Schrödinger equation. Assuming these individual wave functions are $\Psi_1(x, t)$ for $\Psi_2(x, t)$, and the corresponding energies E_1 and E_2, we can generally write:

$\Psi(x,t) = b_1\Psi_1(x,t) + b_2\Psi_2(x,t) = b_1\Psi_1(x)e^{-iE_1t/\hbar} + b_2\Psi_2(x)e^{-iE_2t/\hbar}$, and because the probability density $P(x,t) = \Psi^*(x,t)\times\Psi(x,t)$, it will be time-independent only when $E_1=E_2=E$, which gives $\Psi(x,t) = \left[b_1\Psi_1(x) + b_2\Psi_2(x)\right]e^{-iEt/\hbar}$ such that the time-dependent exponential terms in $P(x,t)$ disappear. Because if $E_1 \neq E_2$:

$$P(x,t) = \Psi^*(x,t)\times\Psi(x,t) = \left|b_1\Psi_1(x)\right|^2 + \left|b_2\Psi_2(x)\right|^2 + b_1^* b_2\Psi_1^*(x)\Psi_2(x)e^{-i(E_2-E_1)t/\hbar} + b_2^* b_1\Psi_2^*(x)\Psi_1(x)e^{-i(E_1-E_2)t/\hbar}$$

becomes time-dependent. So, all you need to do to answer this question is to compare E_1 and E_2.

A. Particle on a ring (2D rigid rotor). The two wave functions describe rotational states with the quantum numbers $m_l = -1$ and $m_l = 2$.

The energy depends on m_l, $E_{m_l} = \frac{\hbar^2}{2I}m_l^{\,2}$, and as a result, $E_{m_l=-1} = \frac{\hbar^2}{2I} \neq E_{m_l=2} = \frac{4\hbar^2}{2I}$.

Therefore the probability density in this case is time dependent – hence this superposition state is <u>not stationary.</u>

You can arrive at the same answer by examining if the wave function $\Psi(x, t)$ is an eigenfunction of the Hamiltonian operator.

Problem 2. Consider a particle of mass μ moving on a ring of radius r. Assume the ring is placed in the x-y plane. The particle is prepared in a superposition state described by the following (unnormalized) wave function: $\Psi(\phi) = \frac{1}{\sqrt{2\pi}}\left[\,7e^{i\phi} - 2ie^{i4\phi} + 6e^{-i7\phi}\,\right]$. Answer the following four questions (questions C and D are on the next page).

A. List all values of the energy of the particle that one can obtain in a single measurement in this state and the corresponding probabilities.

Energies (E):	Probabilities (p):
$\frac{\hbar^2}{2I}$	49/(49+4+36) = 49/89
$\frac{16\hbar^2}{2I} = \frac{8\hbar^2}{I}$	4/89

$\frac{49\hbar^2}{2I}$	36/89

B. Calculate the average value of the energy of the particle that would be obtained as a result of many measurements.

Perhaps the simplest way to answer this question is to calculate the average outcome of multiple measurements using statistical considerations:

$$\langle E\rangle=\frac{\hbar^2}{2I}p_{m_l=1}+\frac{16\hbar^2}{2I}p_{m_l=4}+\frac{49\hbar^2}{2I}p_{m_l=7}=\frac{\hbar^2}{2I}\frac{49}{89}+\frac{16\hbar^2}{2I}\frac{4}{89}+\frac{49\hbar^2}{2I}\frac{36}{89}=\frac{1877}{89}\frac{\hbar^2}{2I}=10.5449\frac{\hbar^2}{\mu r^2}$$

A direct way to answer this question is by using the expectation value equation (4th postulate):

$$\langle E\rangle=\frac{\int_0^{2\pi}\Psi^*(\phi)\left(-\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}\right)\Psi(\phi)\,d\phi}{\int_0^{2\pi}\Psi^*(\phi)\Psi(\phi)\,d\phi}=$$

$$=\frac{\hbar^2}{2I}\frac{\int_0^{2\pi}\frac{1}{\sqrt{2\pi}}\left[7e^{-i\phi}+2ie^{-i4\phi}+6e^{i7\phi}\right]\frac{1}{\sqrt{2\pi}}\left[7e^{i\phi}-2i\times16e^{i4\phi}+6\times49e^{-i7\phi}\right]d\phi}{\int_0^{2\pi}\frac{1}{\sqrt{2\pi}}\left[7e^{-i\phi}+2ie^{-i4\phi}+6e^{i7\phi}\right]\frac{1}{\sqrt{2\pi}}\left[7e^{i\phi}-2ie^{i4\phi}+6e^{-i7\phi}\right]d\phi}=$$

$$=\frac{\hbar^2}{2I}\frac{\int_0^{2\pi}\left[49+4\times16+36\times49\right]d\phi}{\int_0^{2\pi}\left[49+4+36\right]d\phi}=\frac{1877}{89}\frac{\hbar^2}{2I}$$

…

The integration is pretty straightforward, because $\int_0^{2\pi}e^{-im_1\phi}e^{im_2\phi}d\phi=2\pi$ if $m_1=m_2$, and $=0$ otherwise.

C. Calculate the average value of the angular momentum of the particle that would be obtained as a result of many measurements.

The values of the angular momentum ($l_z=m_l\hbar$) obtained in a single measurement:

Values:	Probabilities (same as in Q.A):
$\hbar$	49/89
$4\hbar$	4/89
$-7\hbar$	36/89

Statistical considerations give:

$$\langle l_z\rangle=\hbar p_{m_l=1}+4\hbar p_{m_l=4}-7\hbar p_{m_l=7}=\left(\frac{49}{89}+4\frac{4}{89}-7\frac{36}{89}\right)\hbar=-\frac{187}{89}\hbar=-2.1\hbar$$

As in Q. B, a direct way to answer this question is by using the expectation value equation (4th postulate):

$$\langle l_z \rangle = \frac{\int_0^{2\pi} \Psi^*(\phi)\left(-i\hbar\frac{d}{d\phi}\right)\Psi(\phi)\,d\phi}{\int_0^{2\pi} \Psi^*(\phi)\Psi(\phi)\,d\phi} = \ldots$$

The integration is pretty straightforward, because $\int_0^{2\pi} e^{-im_1\phi}e^{im_2\phi}d\phi = 2\pi$ if m_1=m_2, and = 0 otherwise.

D. Is the particle more likely to be found moving in the counterclockwise direction (positive values of the angular momentum, l_z) or clockwise direction (negative l_z)? *Explain your reasoning and support it by calculations. Tip*: this is a probability question.

The probability to find the particle with the positive value of the angular momentum (rotating counterclockwise) is 49/89+4/89 = 53/89. The probability to find in rotating in the opposite direction is 36/89. Thus, the particle is more likely to be found rotating counterclockwise.

Note that this answer does not contradict the one in question C, because here the question is simply about probabilities, not about the average value which depends on both probabilities and the actual values of the angular momentum.

Problem 3. A quantum mechanical harmonic oscillator with mass μ and force (spring) constant k is in a state characterized by the quantum number $n = 3$. Do the following:

A. (10 points) Write the expression for the wave function $\Psi(x, t)$ of the oscillator. Make sure the wave function is normalized and explicitly includes the time dependence.

$$\Psi_{n=3}(x,t) = A_3 H_3\left(\sqrt{\alpha}x\right) e^{-\alpha x^2/2} e^{-iE_{n=3}t/\hbar} = \frac{1}{\sqrt{2^3 3!}}\left(\frac{\alpha}{\pi}\right)^{1/4} 4\sqrt{\alpha}x(2\alpha x^2 - 3)e^{-\alpha x^2/2}e^{-i7\pi\nu_{HO}t}$$

B. Determine the values of coordinate x where you are unlikely to find the oscillator. *Explain your reasoning*.

Unlikely means $P = |\Psi_{n=3}(x,t)|^2 = [\Psi_{n=3}(x)]^2 = 0$. This happens when $\Psi_{n=3}(x) = 0$, or more specifically, $x(2\alpha x^2 - 3) = 0$, because the exponential factor $e^{-\alpha x^2/2}$ can't be 0.

This means that either $x = 0$ or $2\alpha x^2 = 3$ ➔ $x = \pm\sqrt{\frac{3}{2\alpha}}$. Thus, there are 3 points (nodes) where the oscillator in the state with $n = 3$ is unlikely to be found: one in the center (at the very bottom of the potential well) and two symmetrically positioned at $x = \pm\sqrt{\frac{3}{2\alpha}} = \pm\left(\frac{9\hbar^2}{4k\mu}\right)^{\frac{1}{4}}$.

Problem 4. Your task is to identify and characterize an unknown diatomic molecule X. Here is what you know. When the molecule was placed in a 3D box/cube of size a =5 Å (1 Å=10^{-10} m), the transition from the ground state to the first excited state associated with its translational motion required 1.4169×10^{-23} J of energy. A transition between the ground state and the first excited vibrational state involved 4.3107×10^{-20} J of energy. The force (spring) constant characterizing vibrations in this molecule is 1902 $\text{N}\cdot\text{m}^{-1}$ (1 N=1 $\text{kg}\cdot\text{m}\cdot\text{s}^{-2}$). Answer the following two questions (see next page for question B)

A. Use this information to unambiguously identify the molecule. *Explain your assumptions*. (*Hint:* masses of the atoms in a diatomic molecule can be uniquely identified from the total mass and the reduced mass of the molecule. Consider how the energies of the transitions described above depend on these characteristics.)

The energy of translational motion depends on the total mass (M) of the molecule while the vibrational energy depends on the reduced mass (μ). Therefore you can determine the mass of the molecule from the former and the reduced mass from the latter.

For translational motion, $\Delta E^{trans} = E_2^{trans} - E_1^{trans} = \dfrac{3h^2}{8Ma^2}$, therefore we obtain $M = \dfrac{3h^2}{8a^2}\dfrac{1}{\Delta E^{trans}}$ = 4.6479×10^{-26} kg = 28 amu. (Note that because in a 3D box motions along x, y, z are independent of each other, the first excited state corresponds to an increase in the quantum number for only one of the motions, not all three at the same time.)

With this value of M one can think of two possible di-atomic molecules with the total mass of 28 amu: N_2 and CO. You have no possibility to decide which is the right one based on this value of total M. In order to distinguish between the two you need additional data, in this case the reduced mass.

The reduced mass can be obtained from the information about transition between the vibrational states, assuming that vibrations can be described by the harmonic oscillator model:

$\Delta E^{vibr} = E_1^{tvibr} - E_0^{vibr} = h\nu = \hbar\sqrt{\dfrac{k}{\mu}}$. From here, $\mu = \dfrac{\hbar^2 k}{\left(\Delta E^{vibr}\right)^2}$ = 1.1383×10^{-26} kg = 6.857 amu.

Comparing this result with the expected reduced masses of the two abovementioned molecules (7 amu for N_2 and 6.857 amu for CO), you can now definitively say that the molecule is CO.

For those who are curious: A general rigorous way for determining the masses (m_1 and m_2) of the individual atoms from the total mass M and the reduced mass μ, is to solve the following system of equations:

$m_1 + m_2 = M$

$m_1 \times m_2 = M\mu$

Expressing $m_2 = M - m_1$ from the first equation and substituting it into the second yields a quadratic equation: $m_1^2 - m_1M + M\mu = 0$. Solving this equation gives $m_1 = \left(M \pm \sqrt{M^2 - 4M\mu}\right)/2$ and $m_2 = \left(M \mp \sqrt{M^2 - 4M\mu}\right)/2$. (The presence of two solutions (±) merely reflects the symmetry with respect to which mass is m_1 and which is m_2.) For M = 28 amu and μ = 6.856 amu, one gets (keeping the top signs in the equations): m_1 = 16 amu, m_2 = 12 amu. Therefore we conclude that the molecule is CO.

B. The quantum of energy required for a transition between the ground state and the first excited rotational state of the molecule in gas phase is 7.6785×10^{-23} J. From these data, determine the equilibrium bond length in the molecule. *Explain your assumptions*.

For a rotational transition in gas phase (***assuming* the particle on a sphere/3-D rigid rotor model**):

$\Delta E^{rot} = E^{rot}_{l=1} - E^{rot}_{l=0} = \dfrac{\hbar^2}{2\mu r^2}2 = \dfrac{\hbar^2}{\mu r^2}$, where r is the bond length. The reduced mass of the molecule can be determined from the energy associated with the transition between vibrational states (see Q.A):

$\mu = \dfrac{\hbar^2 k}{\left(\Delta E^{vibr}\right)^2}$ = 1.1383 ×10^{-26} kg (see solution to question A). From here we get

$r = \sqrt{\dfrac{\hbar^2}{\mu\,\Delta E^{rot}}} = \dfrac{\hbar}{\sqrt{\mu\,\Delta E^{rot}}}$ =1.128 ×10^{-10} m = 1.128 Å.